2017 DOE Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Washington, D.C.

A Novel Lubricant Formulation Scheme for 2% Fuel Efficiency Improvement

Project ID: FT024

Northwestern University and Argonne National Laboratory

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June 7, 2017

Overview

Timeline

- Project start date: Jan. 18th, 2014
- Project end date: August 31st, 2017
- Percent complete: 80%

Budget

- Total project funding
  - DOE share: $ 1,000,000
  - Contractor share: N/A
- Funding received in full

Goals/Barriers Addressed

- 2% fuel efficiency requires 30-40 % boundary friction reduction plus other means of friction control.
- Friction should be reduced in the entire lubrication range with high thermal stability.
- Energy efficient additives should not have adverse interaction with existing necessary additives.

Partners

- Northwestern University — Lead
- Argonne National Laboratory

In collaboration with

- Ashland, Inc.
- General Motors

Relevance and Objectives

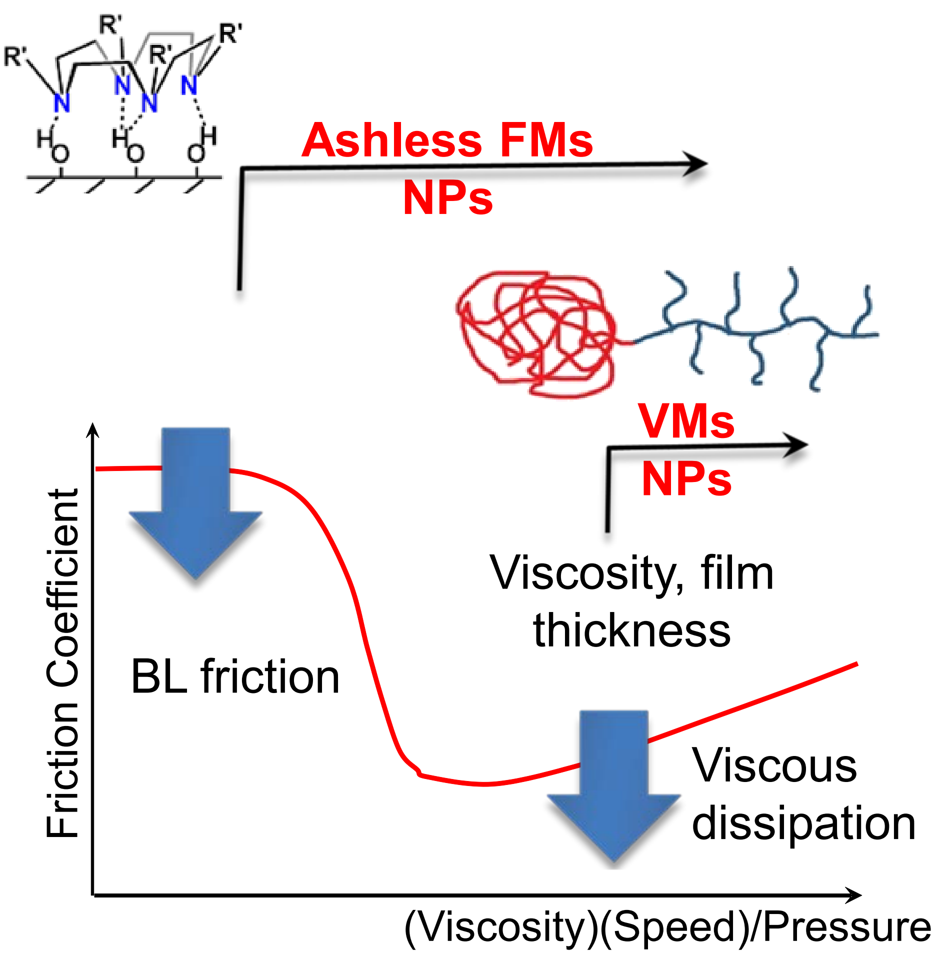
- **Targets**: **Novel energy efficient friction modifiers (FMs), viscosity modifiers (VMs), and nanoparticles (NPs)**.

- **Overall Objective**: Novel lubricant formulations for improving vehicle fuel efficiency by at least 2 % without adversely impacting vehicle performance or durability.
  - Reducing friction due to asperity rubbing in start-up and low-speed;
  - Temporarily reducing the lubricant viscosity (temporary shear-thinning) in medium- to high-speed cruise operations;
  - Suppressing oil aeration or foaming responsible for lubrication breakdown in high-speed operations.

- **FY 16 Objectives** (January 2016 through March 2017)
  - Further improvement of the heterocyclic FMs for boundary lubrication (BL).
  - Design and synthesis of di-block copolymer VMs for low shear at high speeds.
  - Molecular dynamics (MD) modeling of the FMs and VMs, and surface physical/chemical investigations.
  - Surface functionalization of solid-state lubricating NPs for friction reduction and wear prevention.
  - Experiments and confirmation on at least 25-30 % BL friction reduction.

Strategy and Approaches

Key ingredients: FMs, VMs, NPs.



- ❑ Design and synthesis of ashless FMs
- ❑ Synthesis and characterization of di-block copolymer VMs
- ❑ Additive selection via micro-/marco-scale friction tests

- ❑ Nanoparticles on wear reduction

- ❑ Dependency of BL performances on adsorption thermodynamics
- ❑ VMs' thermo-thickening and shear-thinning behaviors
- ❑ Integration of desirable FMs, VMs, and NPs

Modeling

Milestones

Milestone	Status
1. Heterocycle-based FMs, Design and Synthesis Go/No-go Decision: at least 25-30% boundary friction reduction	Complete
2. Temporary Thinning VM Modifiers, Design and Synthesis Demonstration of temporary shear thinning	On Track
3. Nanoparticles in Lubricants and Characterization Go/No-go Decision: no severe wear	Complete
4. Model-Assisted Optimal Molecular and Mixing Design: model developments for the newly synthesized FMs and VMs	On Track
5. Surface Functionalization and FM-Surface Interactions	Complete
6. Tribological and Rheological Properties of Lubricant Formulations	On Track
7. Friction and Wear Tests on Immediate Formulations under Cold Start, Hot-Stop, High Temperature, and High Shear Conditions	Complete
8. Further Tests under Industrial Settings	On Track

Technical Accomplishments and Progress

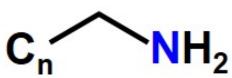
I. Study of the S- and P-free heterocyclic FMs:
- Boundary lubrication friction;
- Boundary lubrication film (slide #11);
- Surface adsorption (slides #12 - #14).

II. Design and development of the di-block copolymer VMs:
- Synthesis approach (slide #15);
- Desirable VM products (slide #16);
- Thermo-thickening and shear-thinning (slide #17 - #18).

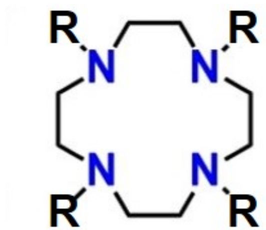
III. Evaluation of the preliminary oil formulations:
- Low-friction performance of FM/VM combination (slide #19);
- Anti-wear property of FM/NPs mixture (slide #20).

Technical Accomplishments and Progress

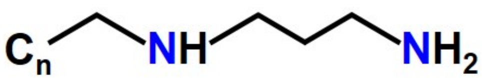
I. Novel thermostable FMs: BL Friction



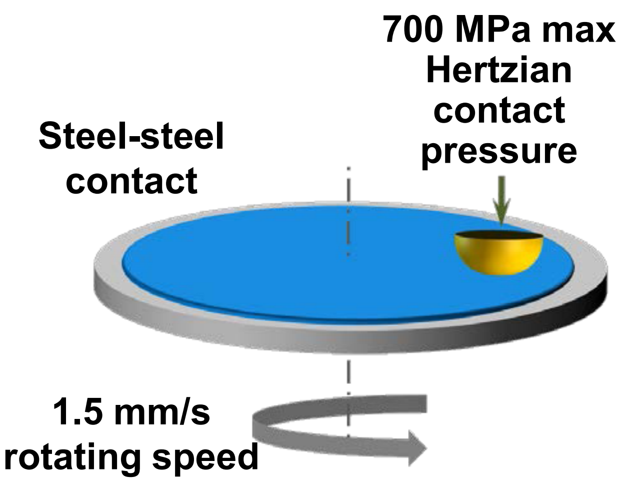
ArmeenT

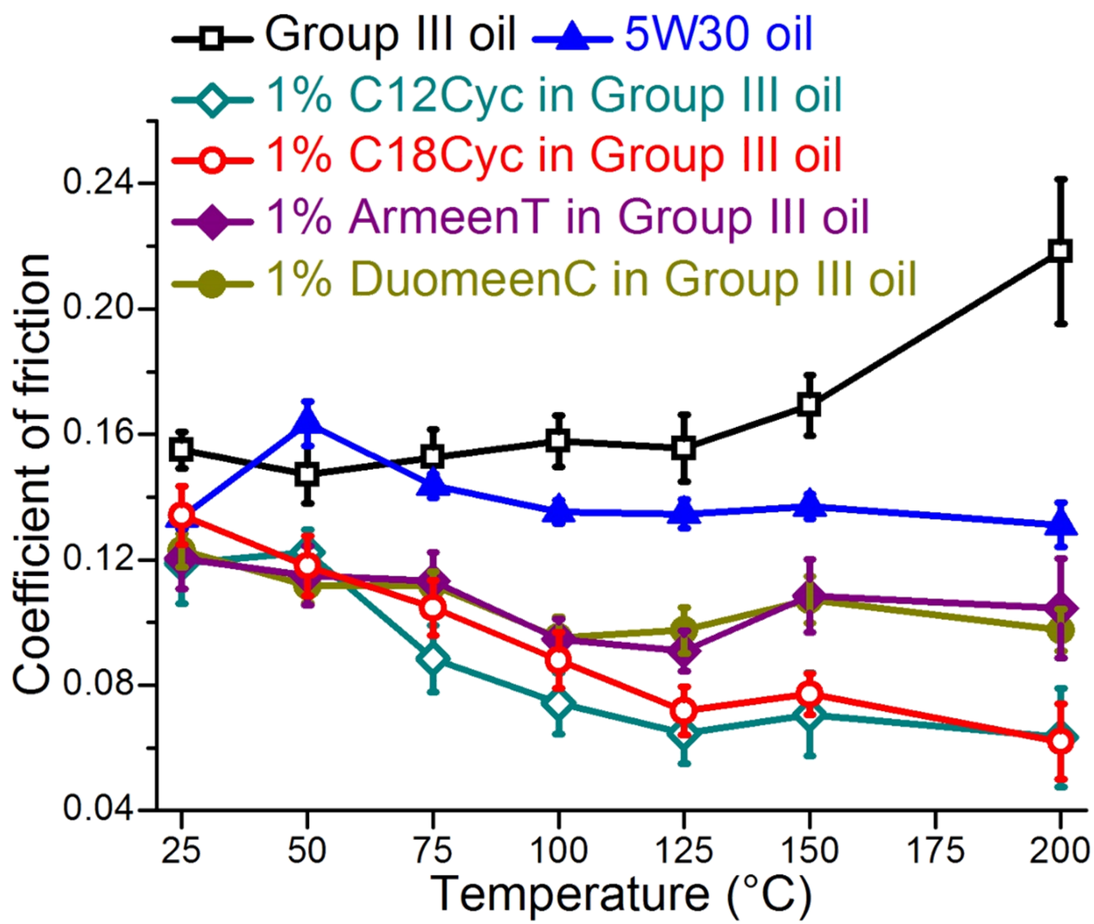


C12Cyc or C18Cyc



DuomeenC

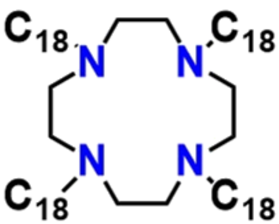




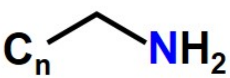
Percentage of BL friction reduction increases from ~ 35 % to ~ 65 % up on heating.

Technical Accomplishments and Progress

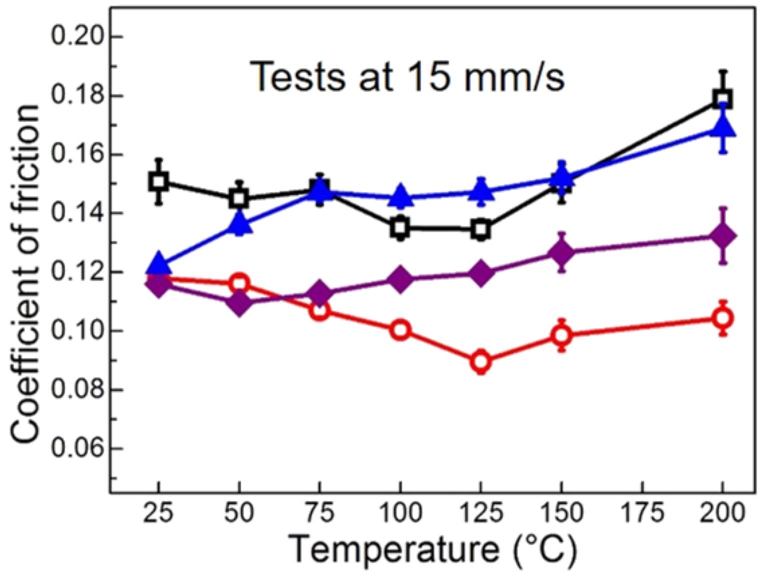
I. Novel thermostable FMs: BL Friction



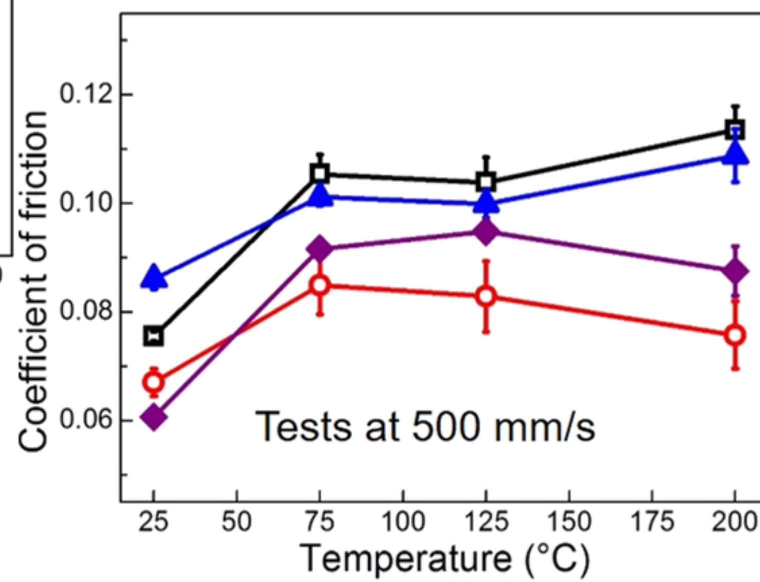
C18Cyc



ArmeenT

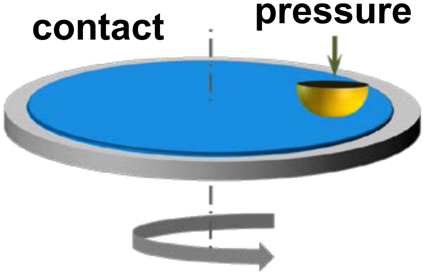


— PAO4 oil — 5W30 oil
— 1% ArmeenT in PAO4 oil
— 1% C18Cyc in PAO4 oil



Steel-steel contact

700 MPa max Hertzian contact pressure

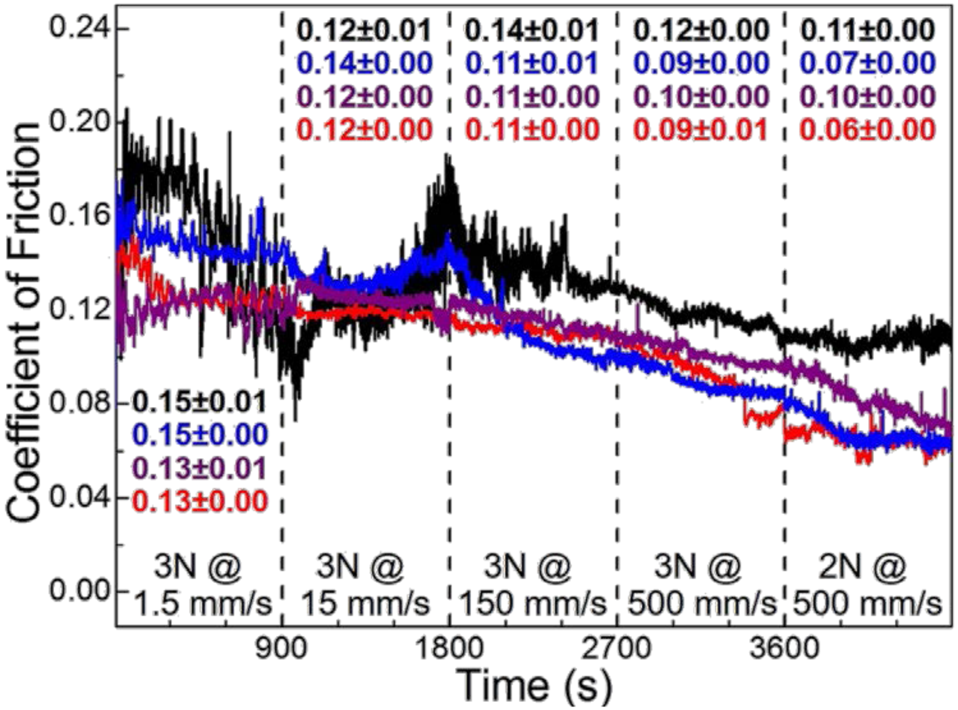


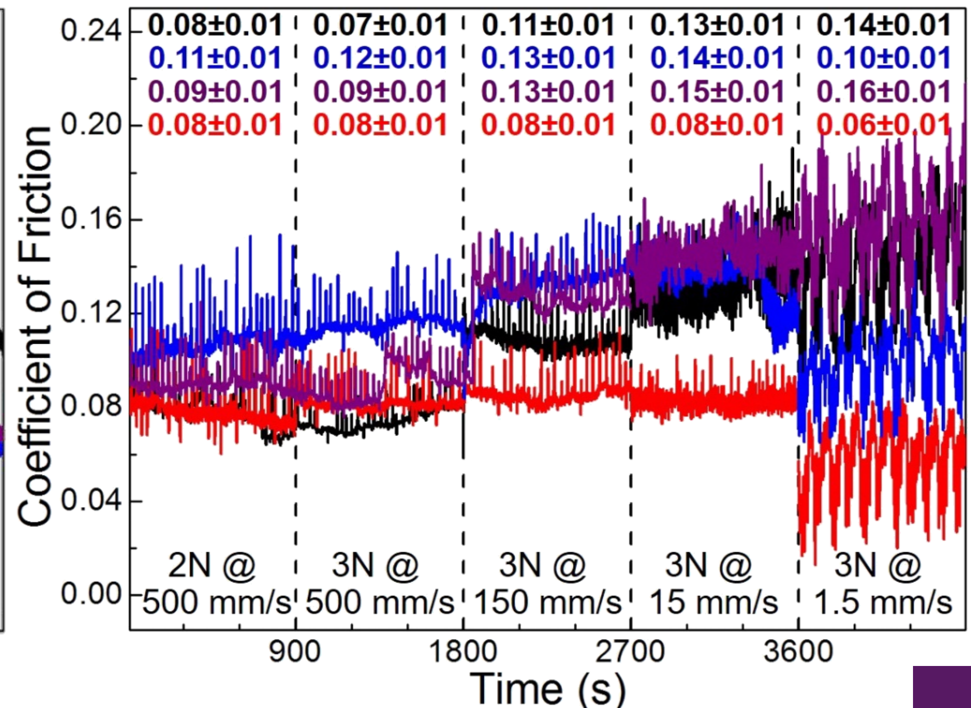
For the high-temperature sliding tests at relatively high speeds, more than 40% friction reduction could be achieved using C18Cyc FM.

Technical Accomplishments and Progress

I. Novel thermostable FMs: Cold-start/hot-stop friction

— PAO4 oil — 5W30 oil — 1% ArmeenT in PAO4 oil — 1% C18Cyc in PAO4 oil





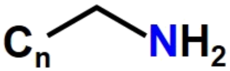
— Speed ramp-up tests at 25 ºC (left) and speed ramp-down tests at 200 ºC (right). More than 60 % friction could be reduced by C18Cyc FM.

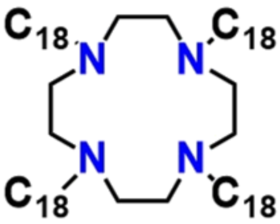
— The heterocyclic FM imparts a great friction reduction capability to the base oil in the cold-start and hot-stop operations.

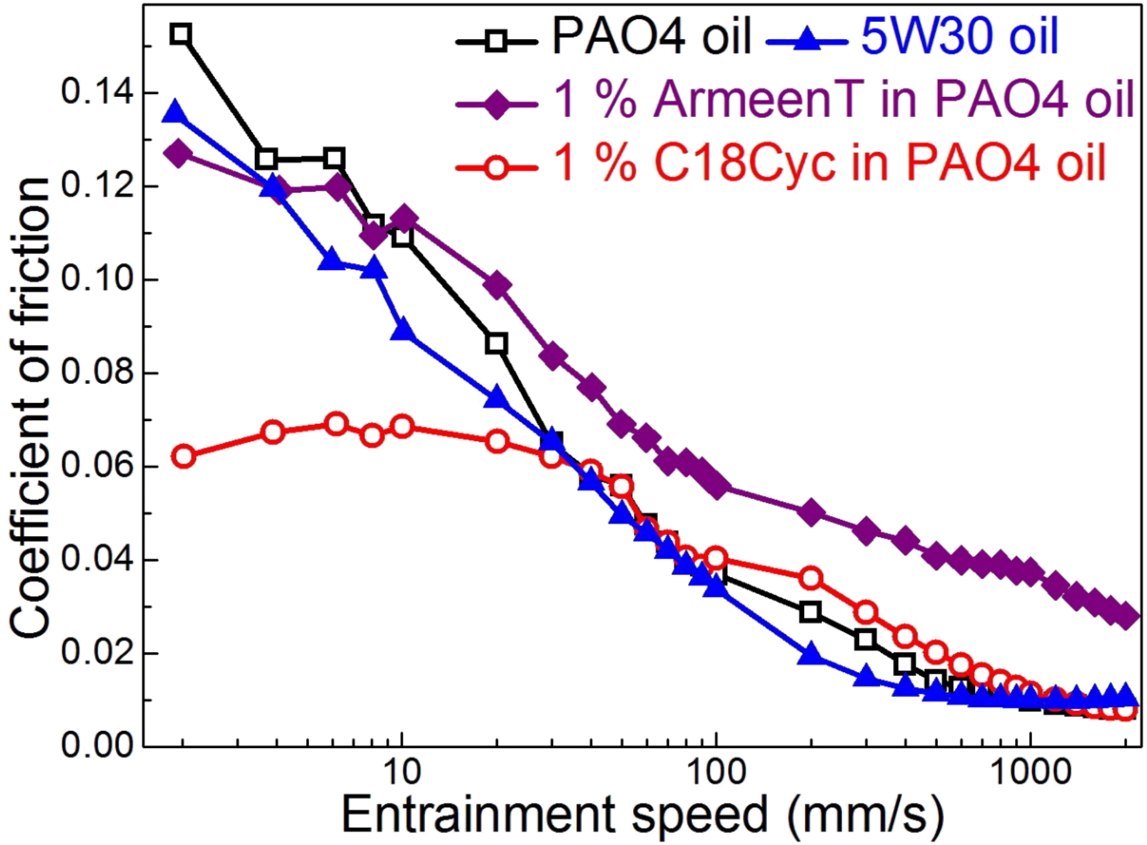
Technical Accomplishments and Progress

I. Novel thermostable FMs: Rolling-sliding friction

50 % S/R, 125 °C, 700 MPa





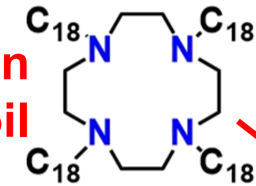


- Up to ~57 % friction reduced in BL regime, which is more than that achieved by the commercial products. Similar performances were obtained under higher contact pressures (1GPa and 1.25GPa)
- The new FM is harmless to hydrodynamic lubrication properties of base oil.

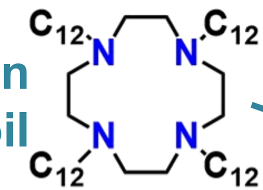
Technical Accomplishments and Progress

I. Novel thermostable FMs: BL films

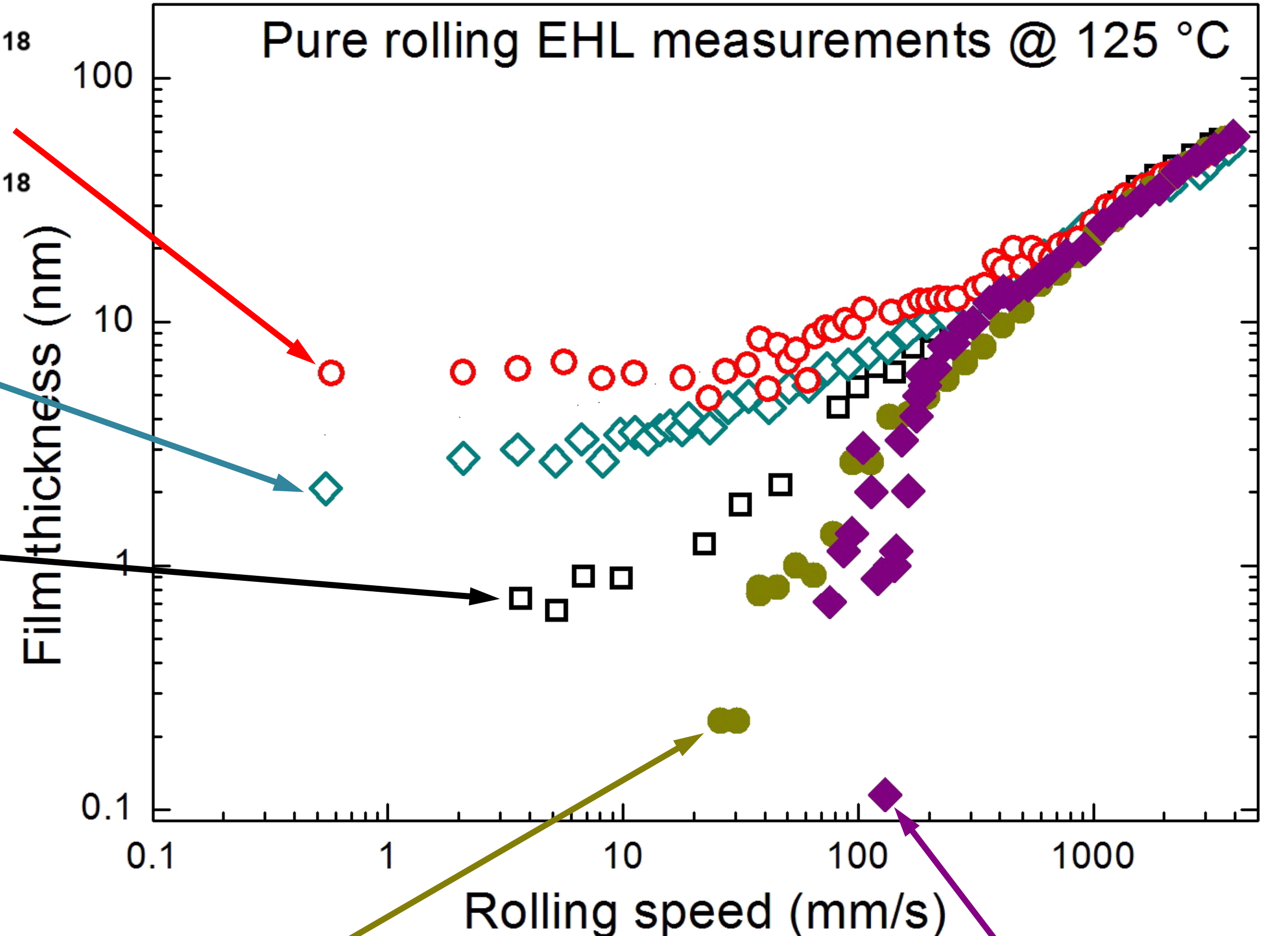
1% C18Cyc in Group III oil

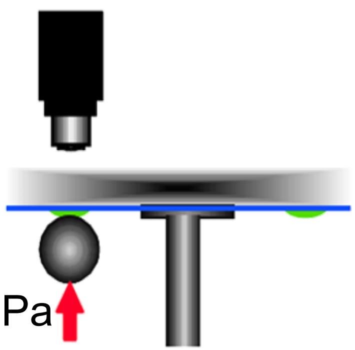


1% C12Cyc in Group III oil

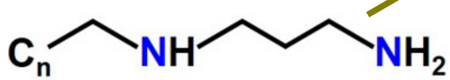


Group III oil

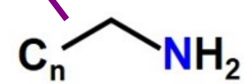




Courtesy of PCS Instruments



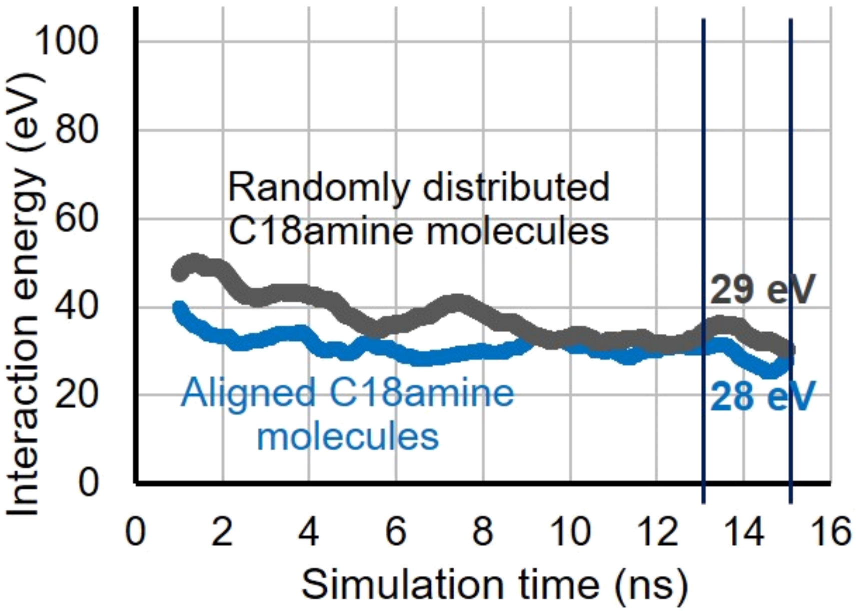
1% DuomeenC in Group III oil

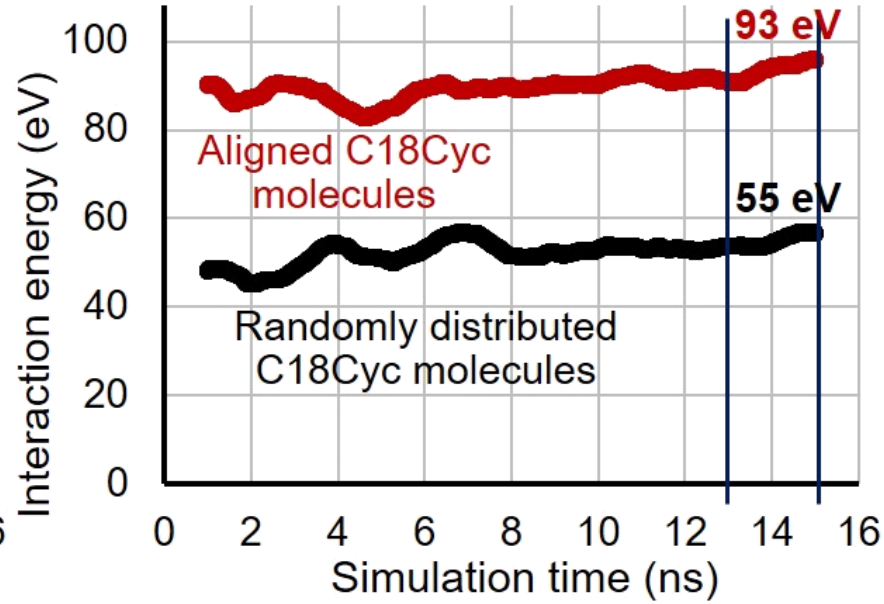


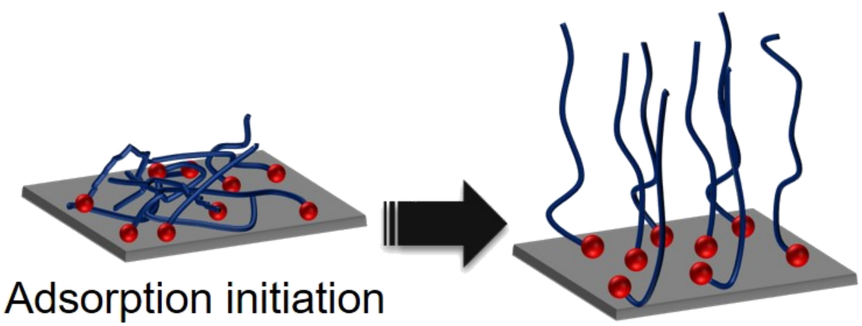
1% ArmeenT in Group III oil

Technical Accomplishments and Progress

I. Novel thermostable FMs: Surface adsorption via MD simulations







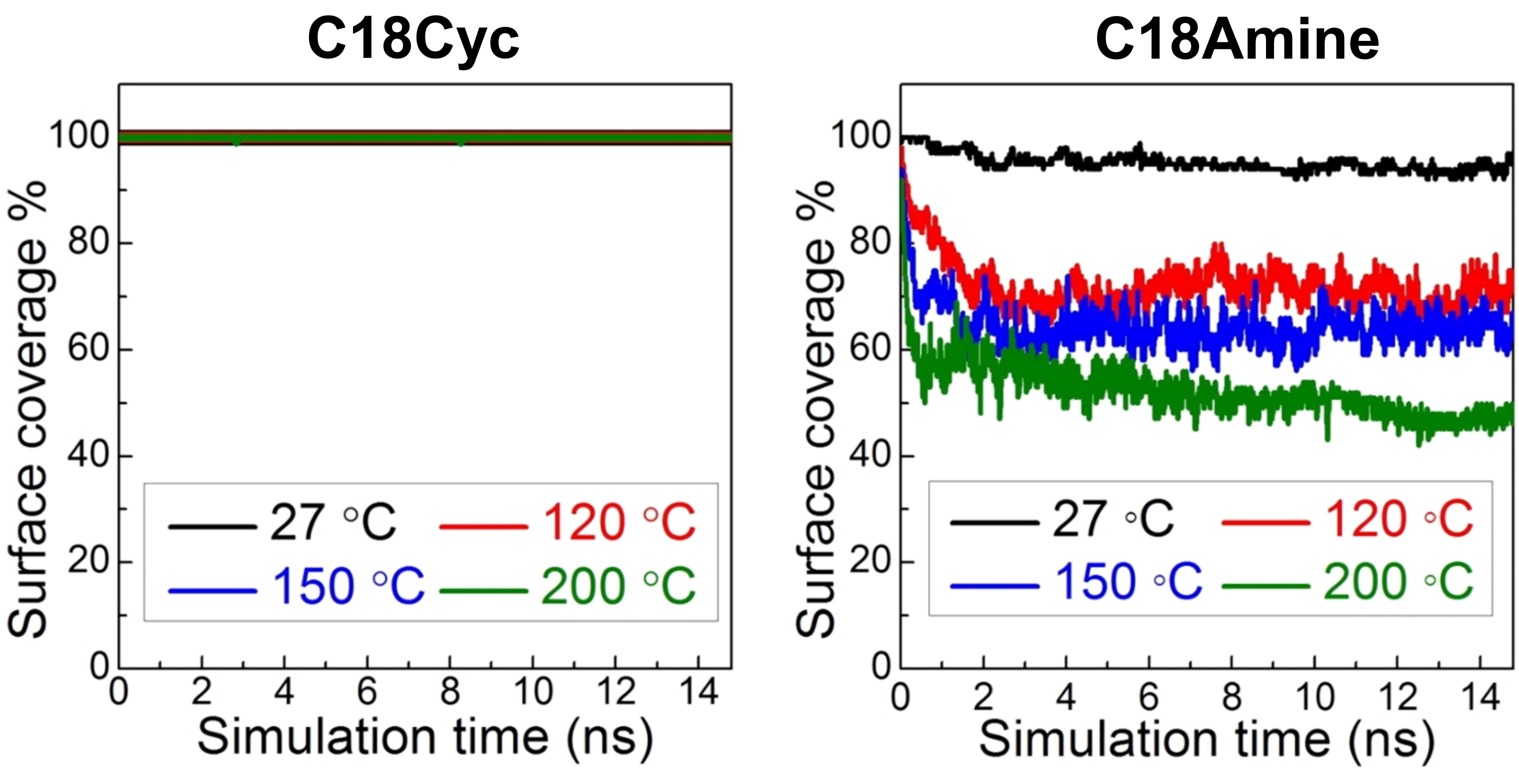
Adsorption initiation (Random model)

Adsorption finalized (Aligned model)

- Already high interaction energies show a visible difference between different models for the new FM, indicating their necessary alignment for an enhanced BL performance.
- Such alignment of the C18Cyc FM molecules improves the surface adsorption.

Technical Accomplishments and Progress

I. Novel thermostable FMs: Surface adsorption via MD simulations



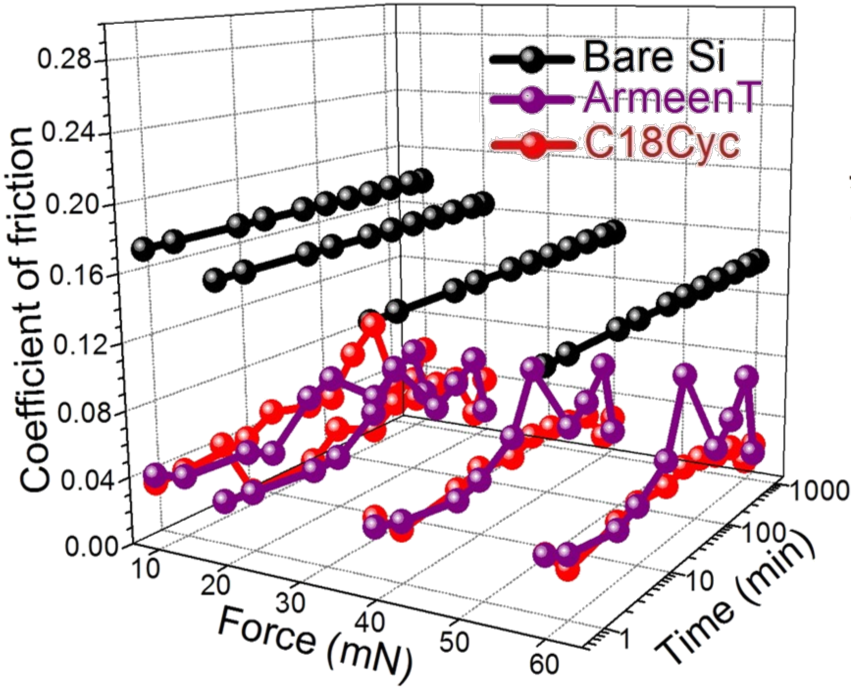
— Surface coverage of the adsorbed C18Cyc molecules does not change with temperature (left), meaning no desorption occurs in this temperature range.

— The adsorbed layer of C18amine molecules deteriorates as temperature increases (right), indicating a desorption process.

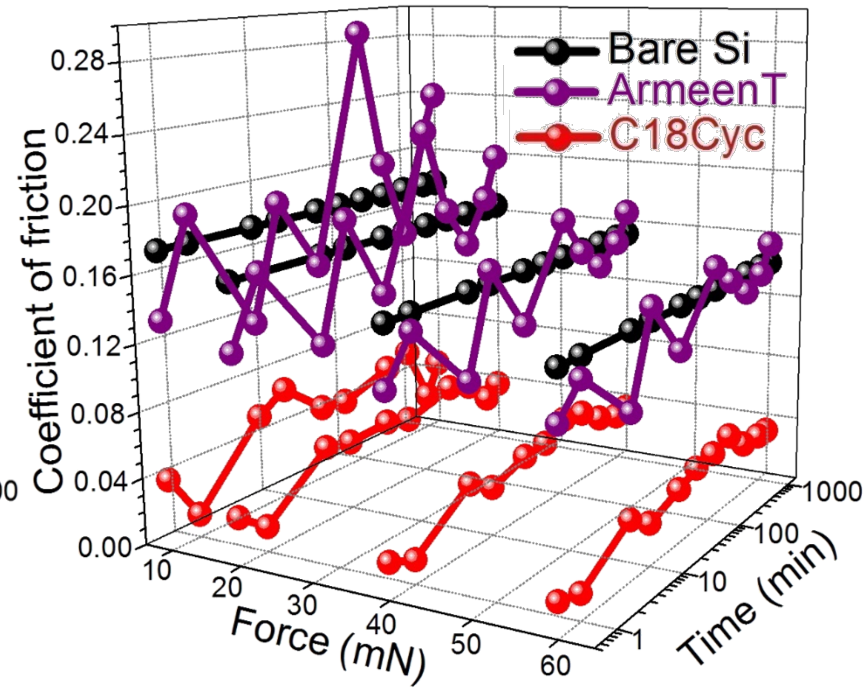
Technical Accomplishments and Progress

I. Novel thermostable FMs: Surface adsorption via Nanoscratch

As-coated samples



Rinsed by toluene after coating



— The weakly bonded ArmeenT molecules are removed by the solvent, and the nanoscratch processes show no reduction of the adhesive friction.
— Well maintained low friction indicates that the heterocyclic FM molecules are strongly adsorbed to the surface and cannot be washed away by the organic solvent.

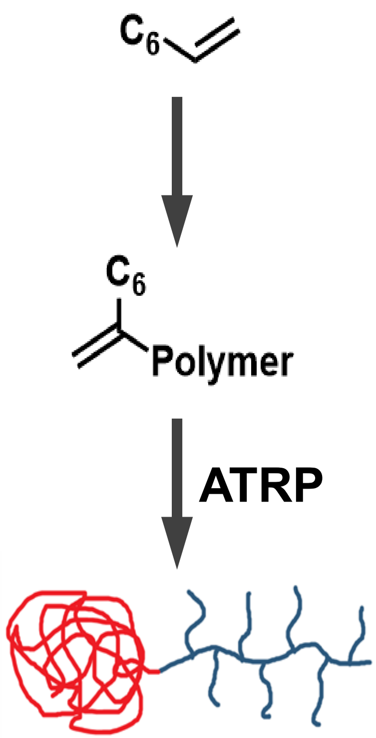
Technical Accomplishments and Progress

II. Di-block copolymer VMs: Synthesis

- **Approach 1: Group 10 polymerization catalysts**
  - Capable of randomly copolymerizing the both blocks.
  - Incapable of homopolymerizing polar monomers.
- **Approach 2: Organolanthanide catalyst**
  - Capable of simply homopolymerizing the both blocks.
  - Only linear polymer with very poor oil solubility obtained.
- **Approach 3: Metallocene catalysis and atom transfer radical polymerization (ATRP)**
  - Succeeding in making the desirable di-block copolymer.
  - A branched polymer block was synthesized first, and a coiled polymer block grew off of it.

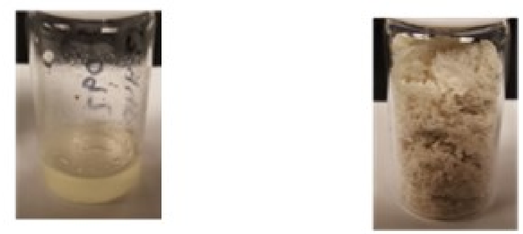
Technical Accomplishments and Progress

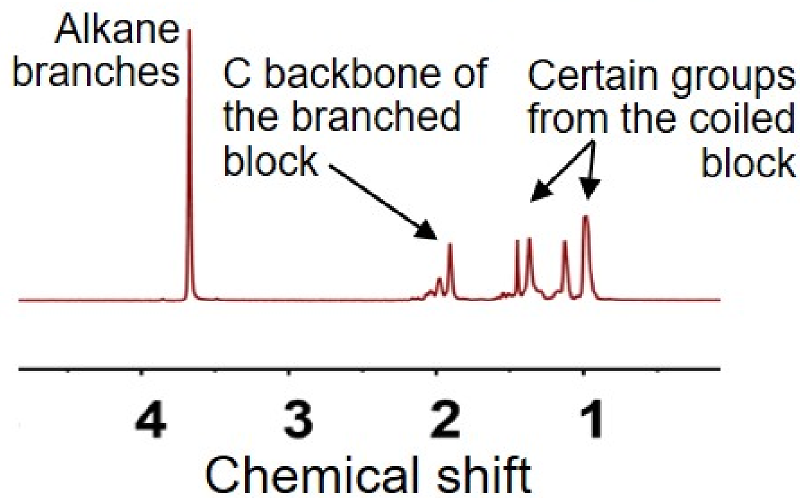
II. Di-block copolymer VMs: Characterization



Coiled Block--Branched Block

Halogen-terminated branched block | Di-block copolymer



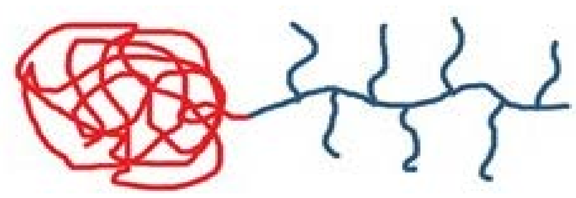


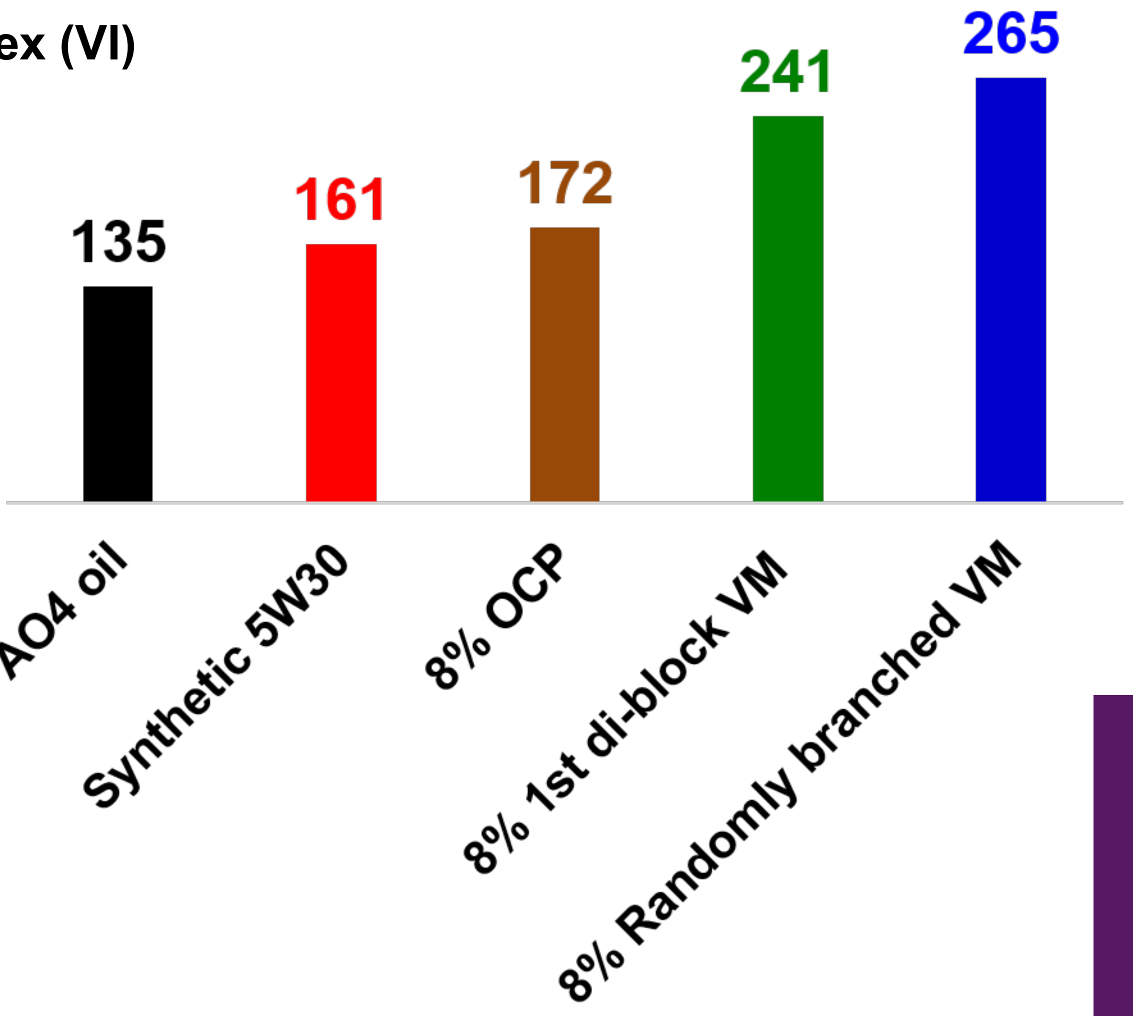
— Proton NMR peaks corresponding to both chemical blocks are observed.
— A visual difference between the two polymers is shown too.

Technical Accomplishments and Progress

II. Di-block copolymer VMs: VI comparison

ASTM D2270 for viscosity index (VI)





Great improvements of VI is obtained by using the newly developed VMs, indicating a desirable thermo-thickening property.

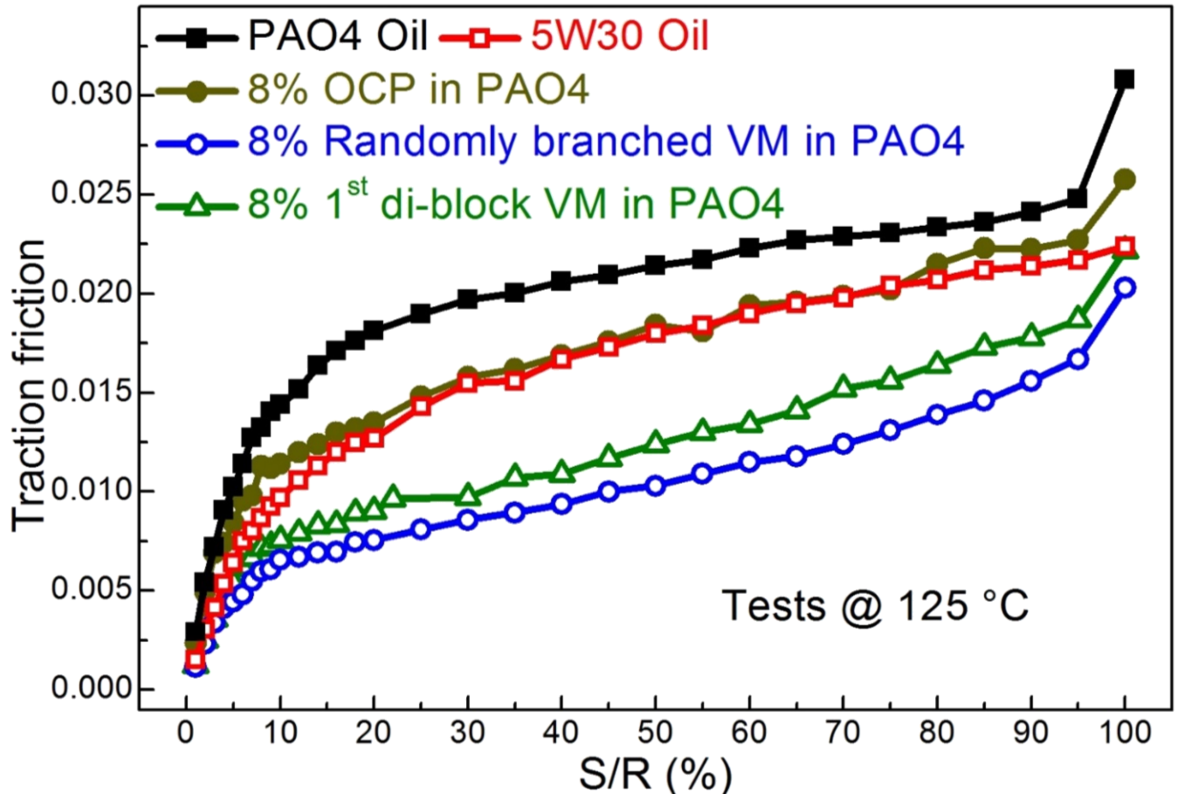
Technical Accomplishments and Progress

II. Di-block copolymer VMs: Traction vs S/R

Speed: 2,000 mm/s

S/R: 1 % — 100 %

P_{max}: 828 MPa



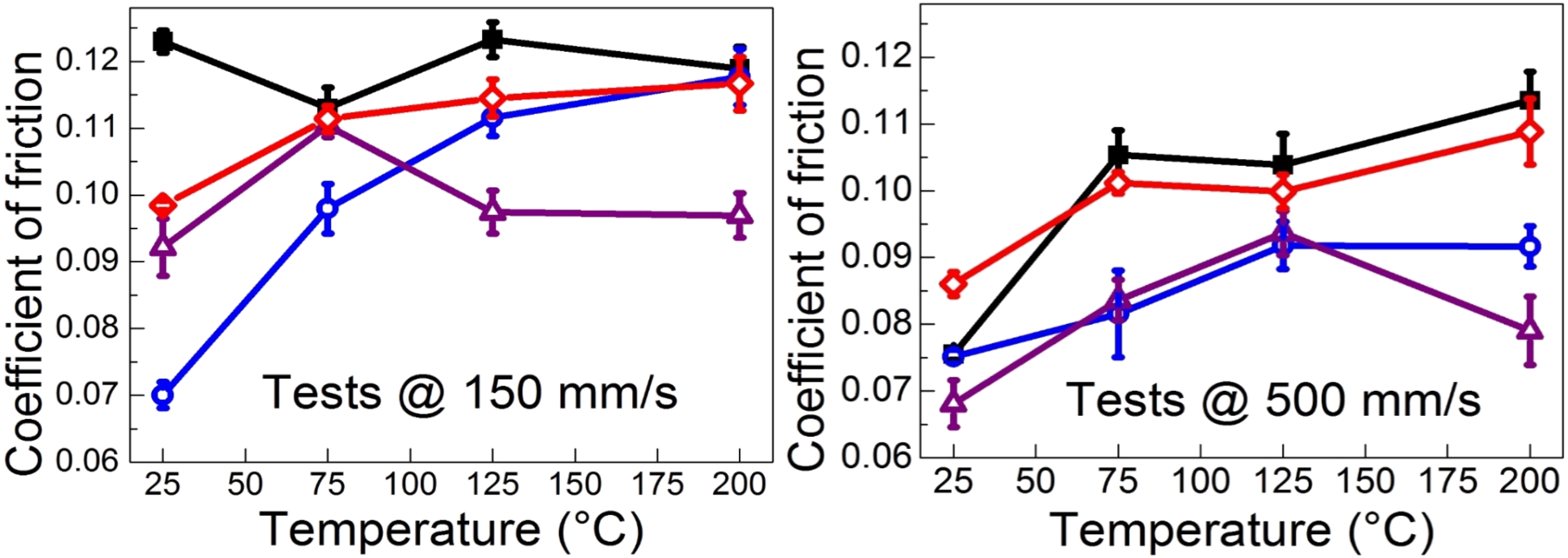
— Significant friction reduction implies an improved shear-thinning process, whose mechanism will also be studied.
— There is a great room for further improvements by modifying the di-block structures.

Technical Accomplishments and Progress

II. Evaluations of a preliminary FM/VM formulation

PAO4 oil — 5W30 oil

— 8% Randomly branched VM in PAO4 — 1% C18Cyc in the VM mixture

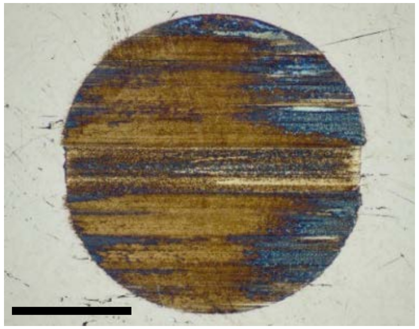


— The new FM makes the new VM mixture work better, especially for the high temperature tests.
— Different additive components in the base oil need to be well balanced for the most optimized tribological performances in future.

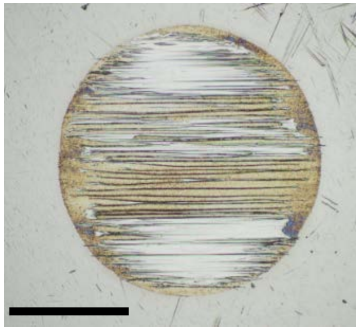
Technical Accomplishments and Progress

III. FM/B_2O_3 NPs mixture: Wear tests at 75 ºC

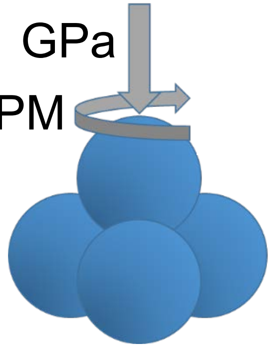
Synthetic 5W30 formulated oil



0.5% NPs in PAO4



Scale bar: 200 µm



	Ball wear x 10^3 (µm^3)
PAO4 oil	3283
0.5% NPs	189
0.5% NPs + 1% C12Cyc	109

- After reciprocating ball-on-flat tests, the oil with NPs results in less wear than the synthetic 5W30 oil, 340E3 μm^3 compared to 490E3 μm^3.
- Based on this NPs-base oil mixture, more four-ball wear tests were conducted.
- The wear performance is further improved through the inclusion of C12Cyc FM with the NPs.

Responses to Previous Year Reviewers' Comments

- **Thermal stability of the nanoparticle functionality group in a combustion environment?**
  Organosilanes used in this research could not be decomposed at a temperature below 400 ºC.
- **Surface competition between FM and nanoparticles for seats?**
  Different additives will be balanced in our future oil formulations for the most optimum performances.
- **Will our FM work on non-ferrous materials?**
  Nanoscratch study of the FMs on DLC and aluminum surfaces are being conducted.
- **Will dispersives in oil affect the FM surface planting?**
  About 20 % extra friction reduction was obtained by adding C18Cyc directly into a fully formulated 5W30 oil in reciprocating sliding tests at 150 ºC without showing adverse effect of dispersives.
- **Will our FM work for degraded oil?**
  Base oils loaded with the new FMs aged at 120 ºC for 125 hours did not show deteriorated anti-friction property.

Collaborations

- **Northwestern University and Argonne National Laboratory**
  - Functionalized nanoparticle tribological studies;
  - High temperature high shear (HTHS) experiments, scuffing resistance tests, and tribo-layer measurements;
- **Ashland, Inc.**
  - Supply of base stocks for tribological;
  - Assistance and guidance in lubricant formulation with the newly-synthesized additives;
  - Tests for oxidation stability and rheology of the new products.
- **General Motors**:
  - Validation of the test results from NU and ANL;
  - Assistance and guidance on the dynamic and thermal effects on lubrication efficiency;
  - Engine tests for fuel consumption and exhaust discharge evaluations.

Remaining Challenges and Barriers

- **Interaction between additives:** Whether any adverse interactions would occur between the newly made or existing additives to be used in an engine oil?
- **Best formulation strategy**: What is the optimal composition of additives for a wide range of temperature and operating conditions for the most friction reduction.
- **Distance between laboratories and industrial applications**: Will the significant friction reduction be converted to significant fuel economy improvement?

Future Work

2017

- **Final synthesis of the lubricant additives**:
  - Synthesis of di-block copolymer VMs with different molecular weights and block distributions;
  - Verification of the di-block copolymer structure by resolving its bridging atoms;
  - Exploration of phthalocyanine derivatives as another potential metal-complexing FM.

- **Oil formulations with the new additives:**
  - Strategy for formulating an optimized oil based on the heterocyclic FMs, di-block copolymer VMs, and functionalized nanoparticles.

- **Further evaluation of the low-friction oil formulations**:
  - Laboratory tests at more severe conditions;
  - Characterizations of tribo-rheological properties and HTHS behaviors with shear stability evaluations.
  - Industrial verification tests;
  - Continuation of the low-friction mechanism study.

Any future work is subject to change based on funding levels.

Summary

Objective: Novel lubricant formulations for improving vehicle fuel efficiency by at least 2 % without adversely impacting vehicle performance or durability.

Approaches:

- Novel friction modifiers, viscosity modifiers, nanoparticles.
- Surface and tribological testing
- Modeling and model-based design

FY 16 Accomplishments

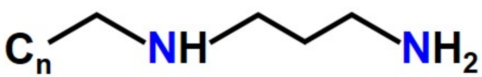
- Among the three generations of heterocyclic FMs developed in this research, the cyclen derivatives have been found to be the best for the BL applications in terms of lubrication improvements, stability, and durability. Its tribological advantages surpass a group commercially available FMs and a fully formulated 5W30 engine oil.
- Surface adsorption and BL film reinforcement are proven to be the principal mechanisms for the BL improvement; the heterocyclic FMs are capable of performing both roles better.
- Group 10, organolanthanide, and metallocene polymerization catalysts were evaluated thoroughly in synthesizing the di-block copolymer VMs with appreciable yields. ATRP with a metallocene catalysis process is proven to be the most suitable approach.
- Tribological improvements by the newly developed VMs were identified as their greatly enhanced thermo-thickening and shear-thinning performances.
- Friction and wear performances of preliminary lubricant formulations were evaluated; more tribological improvements have been confirmed for the new additives or the preliminary lubricant formulations developed in the present research.

Technical Back-Up Slides

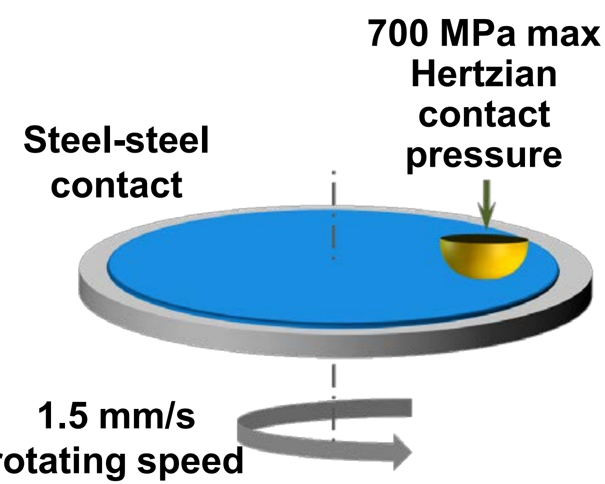
Technical Backup Slides

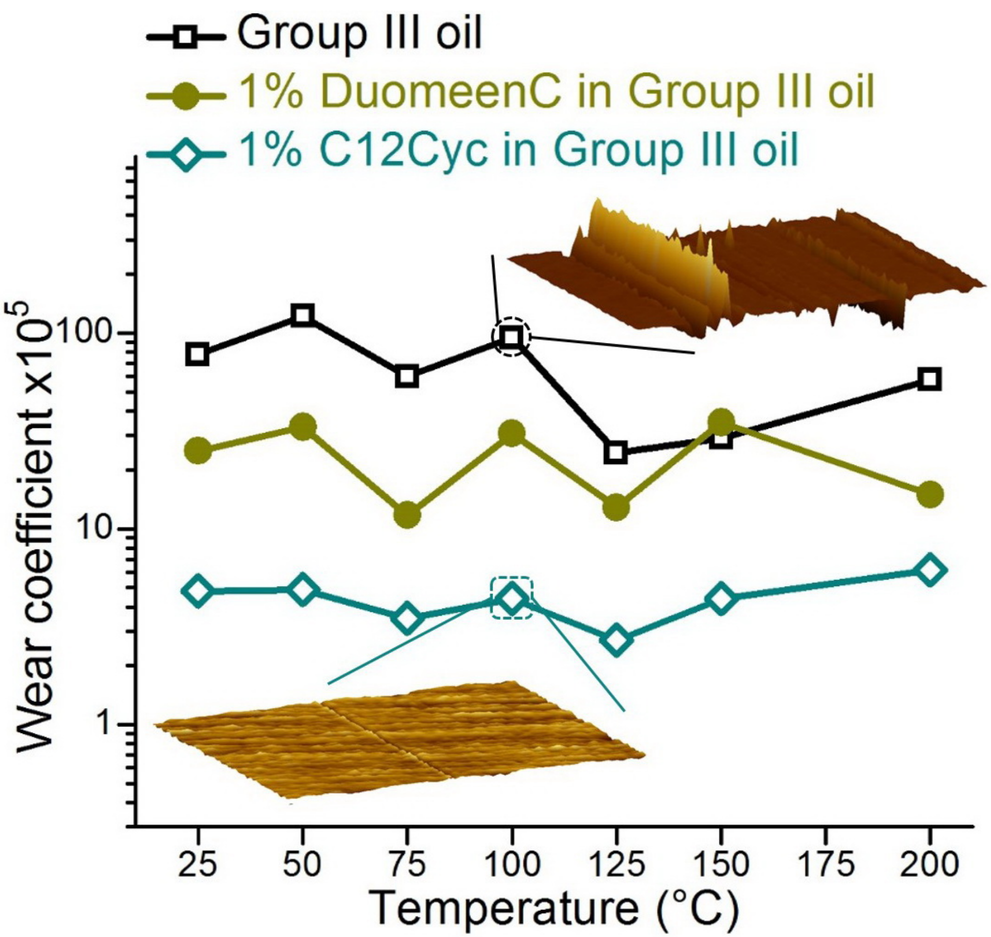
Anti-wear FMs for boundary lubrication

C12Cyc



DuomeenC

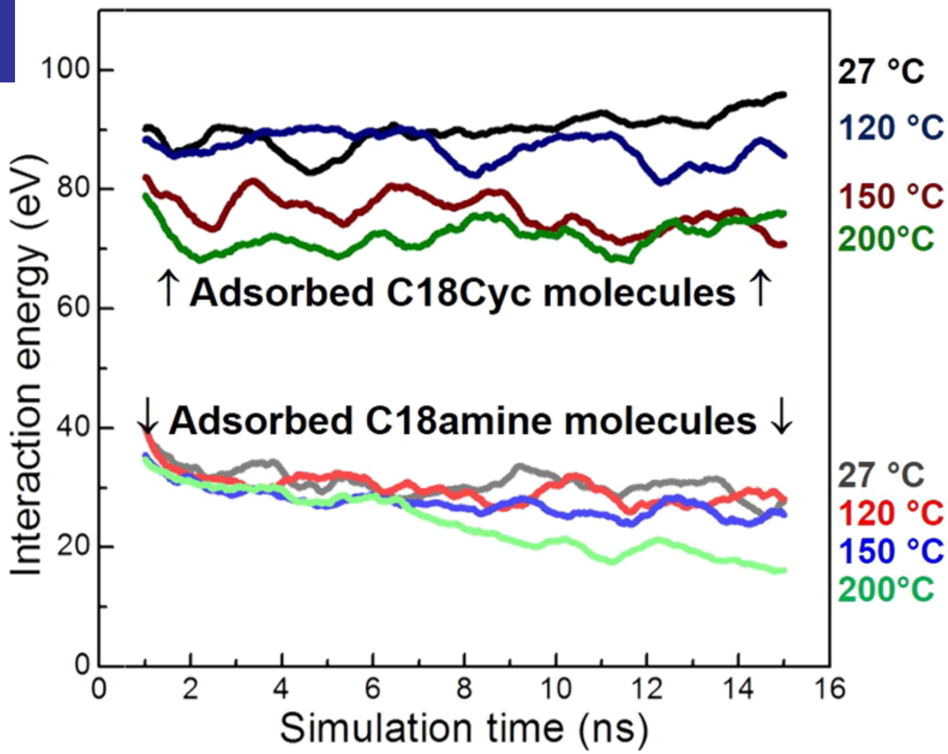


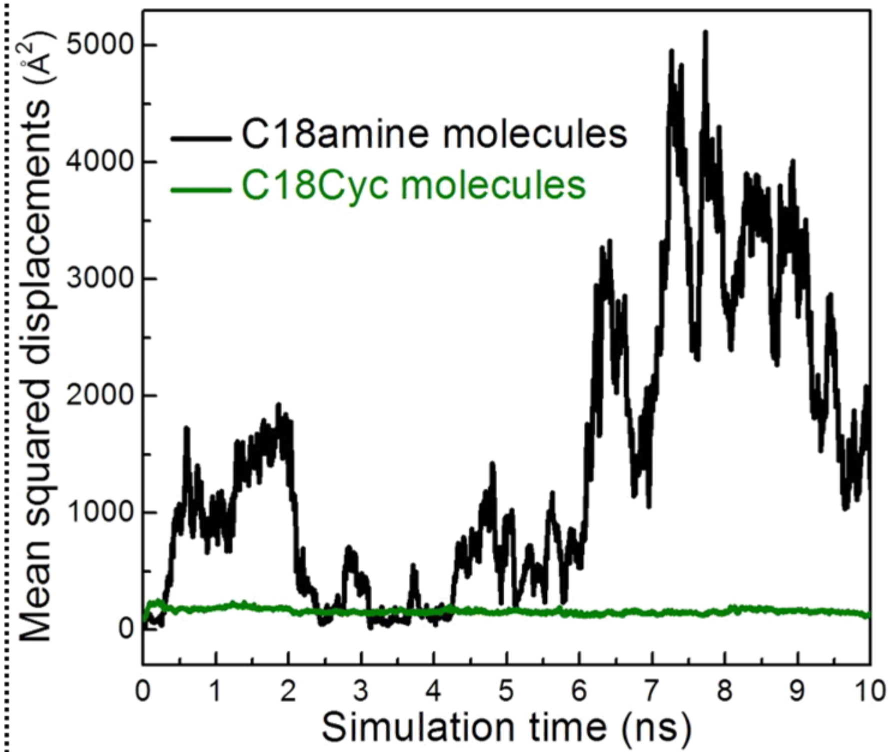


More than one order of magnitude of wear can be eliminated

Technical Backup Slides

Additional MD simulation results



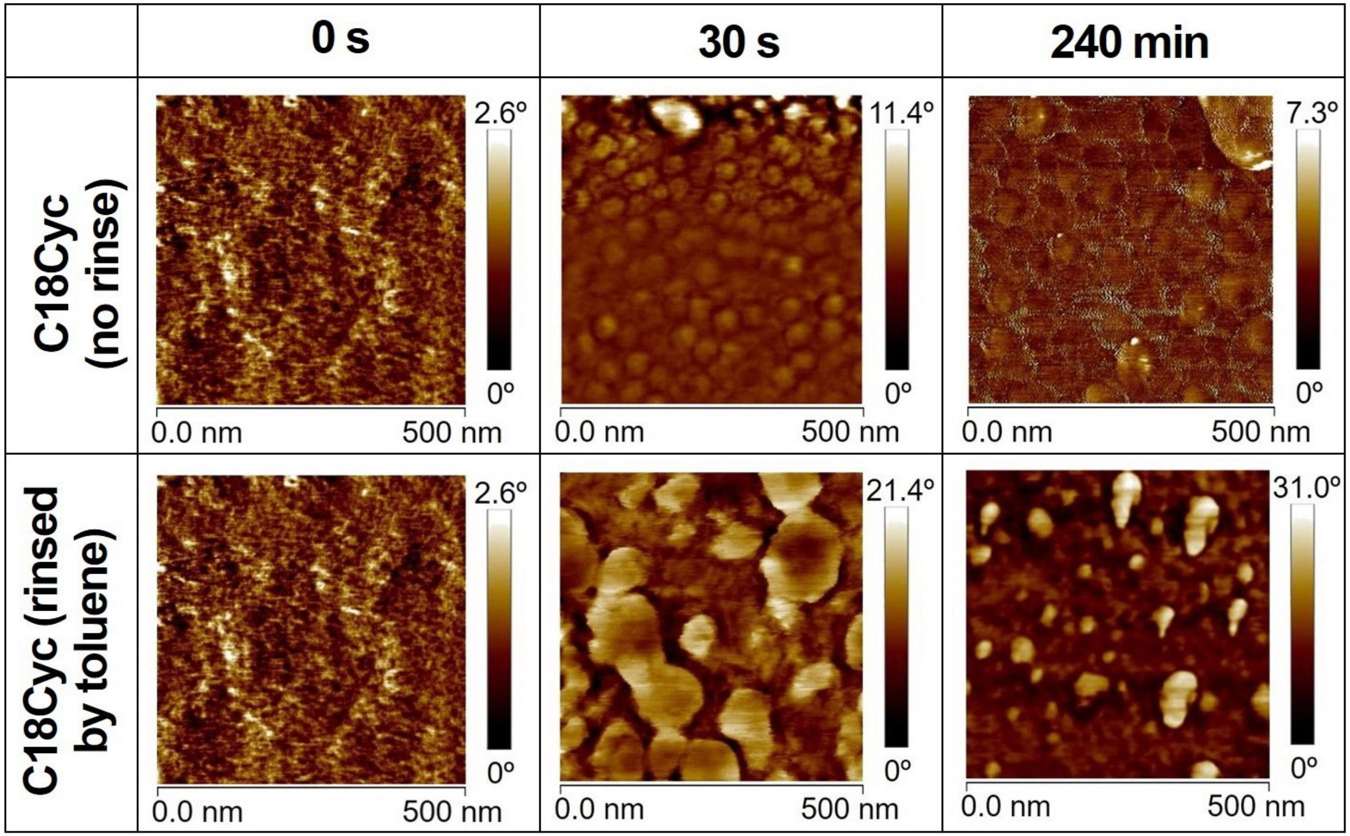


— **The adsorbed C18Cyc molecules have a higher total interaction energy than the adsorbed C18amine molecules.**

— **The average distance C18amine molecules travel on the surface is several orders of magnitude higher than the well adsorbed C18Cyc molecules.**

Technical Backup Slides

Surface adsorption of FM molecules: AFM phase mapping



— **C18Cyc coatings become smooth and uniform after an extended dip-coating process, implying time-temperature dependent surface adsorption.**
— **Rinse-resistance/perdurability of the adsorbed C18Cyc FM is confirmed.**

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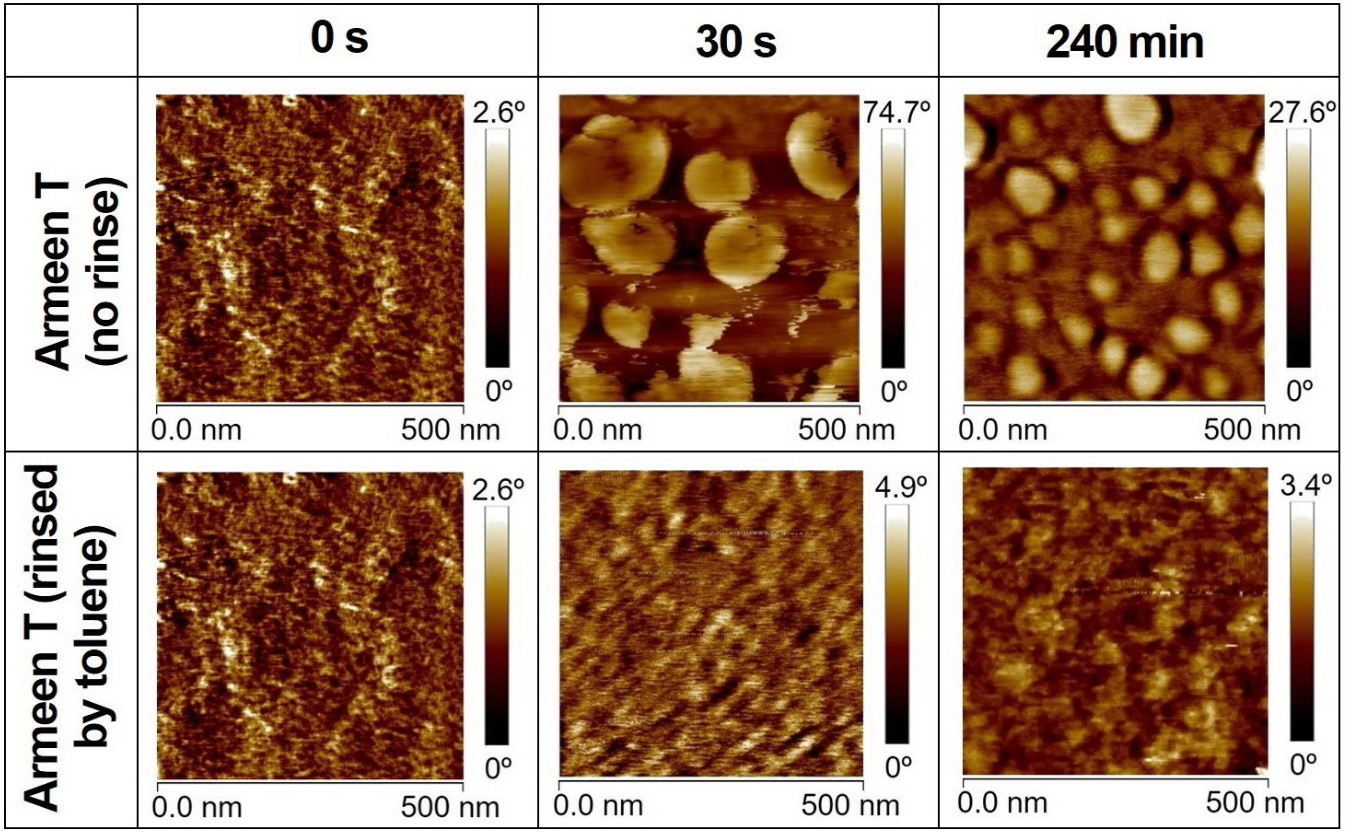

— **Similar phase images to that of the bare silicon surface were obtained after the commercial FM was rinsed.**

— **Adsorption of the ArmeenT molecules is much weaker.**

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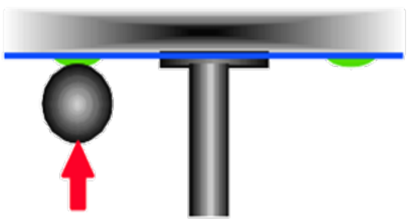
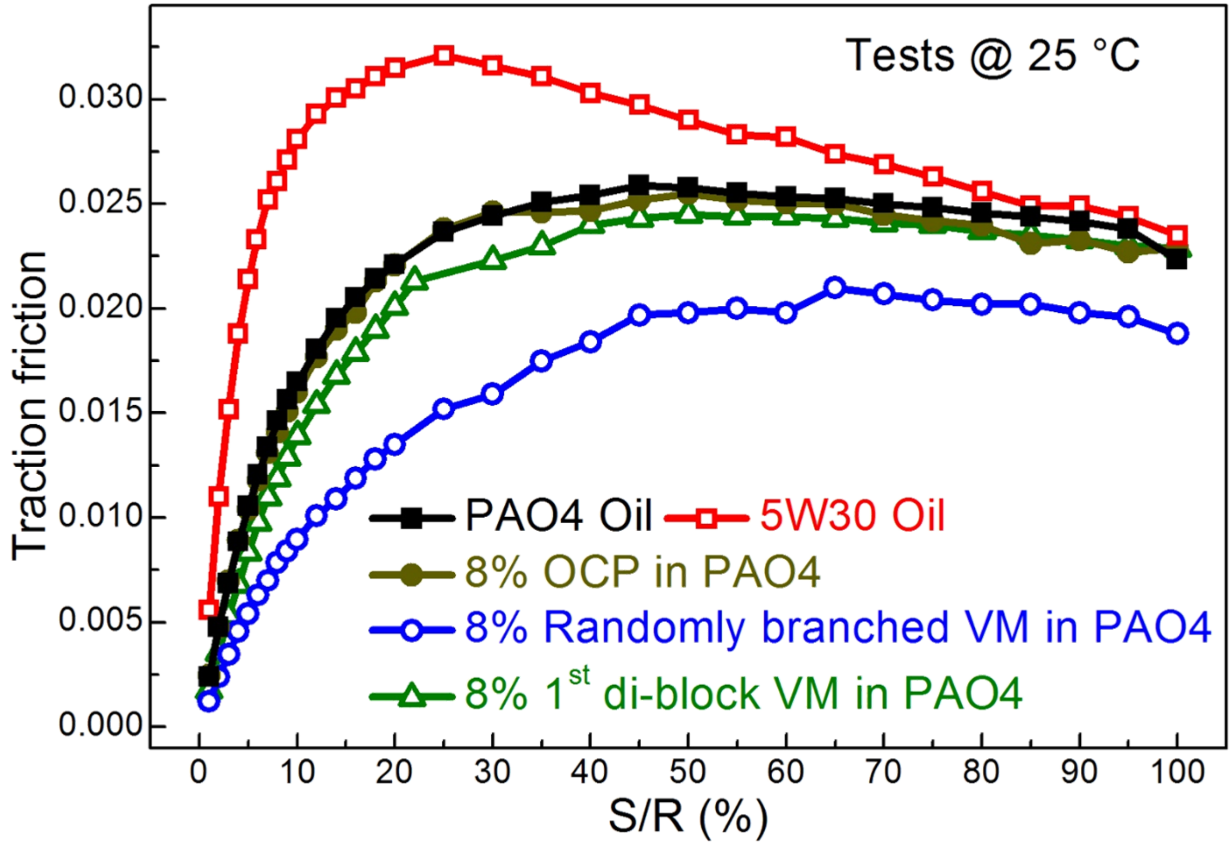
Additional traction friction test results



Speed: 2,000 mm/s

S/R: 1 % — 100 %

P_{max}: 828 MPa



More traction friction could be reduced at room temperature by the new VMs, even though its viscosity is higher than the base oils w/ or w/o OCP VM.